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Radiological Health

RAPID METHODS FOR ESTIMATING FISSION PRODUCT CONCENTRATIONS IN MILK

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

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RAPID METHODS FOR ESTIMATING FISSION PRODUCT CONCENTRATIONS IN MILK

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ABSTRACT

Rapid methods are described for identifying and measuring iodine-131, strontium-89, and strontium-90 in milk by chemical separation combined with counting. The use of multichannel gamma spectroscopy is outlined for determining the gamma-emitting radionuclides cesium-137, iodine-131, and barium-140 in milk.

The method for iodine-131 yields determinations within 2 to 3 hours, and is designed to measure concentrations of 100 μμc/l. The radiostrontium procedure permits analyses of several samples simultaneously in about 5 hours; recovery in tracer studies was found to be 80 ± 5%. The gamma spectroscopy determination is estimated to have accuracy of ± 5 - 10 μμc/l between 0 and 100 μμc/l, and ± 5-10% at higher concentrations.

RAPID METHODS FOR ESTIMATING FISSION PRODUCT CONCENTRATIONS IN MILK

INTRODUCTION

During periods when milk may contain radionuclides in high concentration, their identification and measurement within a few hours is desirable. By combining these measurements with estimates of human milk consumption and the fractional contribution of milk to the consumption of these radionuclides, daily intakes may be computed and compared with ranges recommended by the Federal Radiation Council (FRC)(1). Among fission products having half-lives greater than one week, only strontium-89, strontium-90, iodine-131, cesium-137, and barium-140 are found in milk. Of these, the first three are potentially the most hazardous and should be measured with the greatest care. Based on FRC recommendations and the assumption that milk contributes an appreciable fraction of the daily intake from fresh fallout, it is necessary to measure strontium-90 and iodine-131 at levels of the order of 100 micromicrocuries per liter ($\mu\mu c / l$) of milk and strontium-89 at levels of 1000 $\mu\mu c/l$, and it would be desirable to detect them at one-tenth of these concentrations.

This report is intended to provide relatively simple and rapid methods for identifying and measuring radionuclides in milk. A number of approaches are discussed, and three methods are given in detail. It must be emphasized that these procedures are for warning purposes and, therefore, may yield only approximate values; for precise measurement, methods now in use at the Public Health Service's Division of Radiological Health laboratories and described in the literature (2-4) should be applied. It is hoped that the three procedures described here may permit laboratories relatively new to the measurement of radionuclides to perform milk analyses, and that the introductory discussion will aid them in evaluating other procedures.

The choice of procedure depends largely on available radiation detection equipment and personnel skills. Gross beta and gamma counting require the least skill and the most inexpensive equipment, but they are insensitive and imprecise for identifying specific radionuclides. Radionuclides are

identified and measured most accurately by chemical separation combined with appropriate counting, as described in methods No. 1 and No. 2. Where sufficient funds are available for equipment, multichannel gamma spectroscopy (method No. 3) is recommended for measuring gamma-emitting radionuclides and possibly inferring the concentration of others. An observation of significant radioactivity levels by these three methods should be supported by the analysis of additional samples before control action is taken, and must be confirmed by the more precise methods.

The recommended radioiodine and radiostrontium analyses consist primarily of the separation of these radionuclides from the bulk of the milk on anion and cation exchange resin columns, respectively. The simplicity of the methods depends on the prior elimination of many interfering radionuclides by metabolic processes in the cow. Iodine-131 is the only radionuclide in untreated milk to be retained on the anion resin; therefore, the resin may be gamma counted immediately after the milk has passed through it. Strontium-89 and strontium-90 are accompanied on the cation resin by barium-140, cesium-137, and potassium-40, and are therefore eluted from the resin for separation from the other radionuclides. After purification, they are deposited as a thin sample for gross beta counting. Strontium-89 and strontium-90 are differentiated by counting this sample and then immediately recounting it with an 11 mil aluminum cover which absorbs almost all of the strontium-90 radiation but only approximately one-half that of strontium-89. Their relative concentrations are then computed from the ratio of the two counts.

Single-channel spectrometers with shielded 2" x 2" cylindrical NaI (Tl) crystals and internal proportional counters with shielded 2" diameter chambers, respectively, are used to measure the separated radioiodine and radiostrontium. Detectors with similar or more favorable counting efficiencies and backgrounds may be substituted or larger sample volumes can be used with less effective detectors. In the above systems, 380 μμc of iodine-131 have a count rate of 25 cpm equal to the crystal "background," and 20 μμc of radiostrontium are equivalent to the 30 cpm "background" of the proportional counter. Hence, if count rates equal to counter background are desired at 100 μμc/l levels, one gallon (3.8 liters) of milk is needed to measure iodine-131 and 200 ml for strontium-90. Appreciably lower count rates are statistically significant if the accumulated count is large enough; values equal to background are suggested so that the resulting confirmatory analysis and control action will be based on unambiguous measurements.

Gross gamma measurement of milk for iodine-131 by immersing a scintillation detector in a large volume of milk is an attractive possibility because the apparatus could be mobile, relatively inexpensive, and simple in application. Unfortunately, the count rate of 100 μμc/l of iodine-131 generally is only one-fifth or less of the counter background, and less than one-half of the total count rate of all of the gamma emitters in milk. Hence, the method is insufficiently accurate for iodine-131 at 100 μμc/l levels, even though uncertainty in gross gamma values can be reduced by long counting periods, and the fraction of counts attributable to iodine-131 can be estimated by an experienced analyst. The method becomes very useful for observing trends when fission product levels reach the order of magnitude of 1000 μμc/l. It is inapplicable for measuring strontium-89 and strontium-90 in milk because these radionuclides do not emit gamma rays.

Gross beta counting is also inappropriate for measurements at the 100 μμc/l level, despite the more favorable ratio of counter efficiency to background and the emission of beta particles by all three significant radionuclides. The 1200 μμc/l of naturally-occurring potassium-40 is a high beta "background" within every milk sample, and normal variations in these levels preclude use of a milk "blank" containing no fallout in estimating radiostrontium or radioiodine at 100 μμc/l. For higher levels, the procedure becomes applicable, although care must be taken in evaporating the sample so that the radionuclides are not lost by splattering, or in the case of iodine-131, by volatilization.

Multichannel gamma spectroscopy (method No. 3) is rapid and simple, but appreciable time must be devoted to calibration, maintenance, and calculation. For the three fission product gamma emitters and potassium-40, only four channels are required, although as many as are available can be used. The sensitivity for 100-minute counting periods is approximately 10 μμc/l for 3.5 liter samples if care is taken to minimize channel draft and obtain pertinent "backgrounds." As indicated, two alternative procedures may be followed after calibration with standard solutions of the four radionuclides: (1) the spectrum of the unknown sample is plotted, the "background" and then the standard spectra are fitted to their characteristic peaks in the unknown, one at a time, beginning with the most energetic peak, and then subtracted from the unknown until nothing remains; or (2) four equations, one for each peak, are written to contain the contribution of the characteristic peak, interference from the

three other radionuclides, and "background"; these are solved simultaneously. While similar counter systems will have similar characteristic curves or coefficients, it is important to calibrate every counter individually in order to avoid serious errors. It should be noted that the spectrum and coefficients given for barium-140 include its daughter lanthanum-140 in equilibrium; under conditions requiring the use of the methods given here, the lanthanum-140 would not have grown into equilibrium in the milk during the 10 to 30 hours since the previous milking. Hence, the barium-140 standard should conform to this.

Because of the simplicity of multichannel gamma spectroscopy, once such a system is available, it would be convenient to be able to infer the concentration of such potentially hazardous non-gamma emitters as strontium-90 from the levels of gamma-emitting radionuclides. The use of a cesium-137/strontium-90 ratio has been proposed because both have an approximate 30 year half-life and a similarly high fission yield, and they are found together in many environmental samples, including milk. Careless use of such a ratio would lead to meaningless results, in view of recorded values between 0.5 and 50, depending on the age of the fission products and their path through the environment into the cow. However, considering only foliar deposition and assuming that this is high compared to radiocesium and strontium in feed taken up from the soil, a factor of five should provide a preliminary estimate of strontium-90 concentration. Strontium-89 levels may be based on similar considerations, with a cesium-137/strontium-89 ratio of 0.03 at the time of fission and doubling every 51 days from that moment because of the short half-life of strontium-89. Radiochemical analysis is definitely necessary before taking any major action.

A number of other rapid methods undoubtedly are or will become known. It is suggested that inquiries concerning the use of the accompanying methods or of new methods, the operation and utilization of counters, and the availability of standards be addressed to:

Technical Operations Branch
Division of Radiological Health
U. S. Public Health Service
Washington 25, D. C.

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(4) Porter, Charles, et al.: "Determination of Strontium-90 in Milk by an Ion Exchange Method," Analytical Chemistry, 33:1306-8 (September 1961).

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RAPID DETERMINATION OF IODINE-131 IN MILK

by

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Iodine-131 in market milk is mostly in the inorganic form as the iodide, very little being bound by proteins (1, 2). Of the several fission products formed from nuclear weapons tests or reactor accidents, iodine-131 is the only anionic radionuclide present in milk (3). Therefore, it is possible to absorb iodine-131 on anion exchange resins and determine its activity by gamma counting without interference from other radionuclides, unless formaldehyde has been added or prior cation-exchange resin treatment has been used. Iodine-131 gamma activity is easily measured with a shielded 2" NaI (Tl) crystal with photomultiplier assembly fed through a cathode follower and connected directly to a decade scaler. If a single-channel spectrometer is available, the detector background-to-efficiency ratio may be reduced appreciably by counting only the 364 Kev photoelectric peak.

Experimental

MATERIALS AND APPARATUS

A glass column (3 cm dia x 15 cm) with extra coarse fritted-glass disc at bottom

1-gallon polyethylene bottle

3-oz widemouthed polyethylene bottle

Connecting rubber tubing and glass tubing

Anion exchange resin, strongly basic quaternary amine type, 20-50 mesh size, in chloride form, washed with distilled water (Dowex 2-X8 (Cl^-) has been found very satisfactory)

Counting facility: 2" NaI (Tl) crystal, photomultiplier tube, decade scaler, etc.

Iodine-131 tracer for calibration

PROCEDURE

1. Pour 50 ml of anionic resin into the glass column with the help of distilled water.

2. Place 1 gallon of fresh raw or processed milk (with no preservative added) in the reservoir.

3. Allow milk to flow through the column at 40-50 ml/min flow rate.

4. After all the milk has passed through the column, pour in some warm distilled water and resuspend the resin.

5. Wash the resin with 200-300 ml of warm distilled water until free of milk residue.

6. Transfer the resin quantitatively to a 3-oz widemouthed polyethylene bottle.

7. Determine iodine-131 activity by gamma counting.

DETERMINATION OF COUNTER EFFICIENCY

The efficiency of the counter assembly is a function of geometry which should be maintained constant if the samples are to be compared; if the sample size varies, then the counter should be calibrated for varying sample size. Standard samples of iodine-131 are available commercially for establishing this factor.

Method:

1. Graduate the 3-oz widemouthed polyethylene bottle used for counting samples at varying volumes, such as 10, 20, 30, 40, 50 ml.

2. Transfer a measured amount of iodine-131 tracer of known activity (disintegrations/min) to the bottle.

3. Determine the counting rates (counts/min) of solution after diluting to the desired volumes.

4. Compute the efficiency by dividing observed counts/min by the known disintegrations/min.

5. Construct a graph relating counter efficiency as a function of resin volume. This curve may be used to obtain counter efficiency in the determination of iodine-131 in the unknown samples.

TREATMENT OF DATA

Convert the count rate of a sample to μμc/l:

$$I^{131}\ \mu\mu c/l = \frac{\text{net counts/min}}{2.22\ ERV},$$

where E is the fractional efficiency[1] of the counter, R is the fractional recovery, V is the milk volume in liters, and 2.22 disintegrations/min are equal to 1 μμc.

Comments

This method has been designed to measure levels of 100 μμc/l in milk. In tracer studies, 100 ± 2% of the iodine-131 in milk was retained on the resin from 1 gallon of milk; however, in milk labeled in vivo, the portion of iodine-131 that is protein bound will not be available for ion exchange reactions. Temperatures ranging from 0-30° C have no effect on the absorption of iodine-131 on the column, indicating that cold milk may be used. Milk flow rates up to 1 ml/min/ml of resin will not seriously affect iodine-131 absorption (2). The determination may be made in less than 2-3 hours. The results obtained on milk samples contaminated with fresh fallout by this rapid method and by gamma spectrometry are comparable as shown in table 1.

Table 1.-Iodine-131 Content of Milk as Determined by Rapid Method and Multichannel Analyzer

(Concentrations in μμc/liter)

Sample	Rapid method		Multichannel analyzer (1)
	Gross gamma counting	Single channel analyzer[a]	
1	44 ± 4	46 ± 3	49 ± 9
2	35 ± 3	36 ± 2	39 ± 8
3	23 ± 3	26 ± 3	26 ± 8
4	82 ± 3	81 ± 4	83 ± 8
5	72 ± 3	70 ± 4	68 ± 8
6	41 ± 3	38 ± 3	37 ± 8

[a] Resin placed in a 50 ml lusteroid tube and counted in a well-type (3" x 3") NaI (Tl) crystal.

[1] Counts per disintegration

References

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(3) Squire, H. M., et al.: "The Metabolism by Dairy Cows of Fission Products from Operation Buffalo," United Kingdom Atomic Energy Authority Report T 57/58 (1959), p. 119.

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RAPID DETERMINATION OF STRONTIUM-89 AND STRONTIUM-90 IN MILK

by

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The measurement of total radiostrontium in milk is based on the essentially complete absorption of strontium on cation exchange resin (1, 2). After collecting strontium and other cations on the resin column, they are eluted with sodium chloride solution. Strontium and barrium carriers that were added and other insoluble carbonates are precipitated to separate the strontium from cesium-137 and potassium-40. The precipitate is dissolved and strontium nitrate is precipitated with fuming nitric acid. After dissolving it in water, a barium chromate precipitation at pH 5 removes barium-140. Strontium, together with very little calcium, is reprecipitated with fuming nitric acid. The nitrates are dissolved in water, transferred to a steel planchet, and dried. The sample is measured in a beta counter, and the sample is covered with a thin aluminum foil and recounted to differentiate between strontium-89 and strontium-90.

Reagents and Apparatus

Cation-exchange resin, sulphonated polystyrene type (strong acid), sodium form, 50-100 mesh, -X8 (Dowex 50W -8X, 50-100 mesh, was used in this study)

> NOTE: Prepare resin by washing the cation-exchange column with 1 liter of 4 N NaCl solution and then with 500 ml of distilled water.

Glass reservoir (a 500 ml separatory funnel)

Glass column with extra coarse fritted-glass disc (the column should be approximately 4 cm in diameter)

Ammonium acetate buffer: 1:1 mixture of 6M CH_3COONH_4 and 6 M CH_3COOH

Sodium carbonate: 3N

Nitric acid: 6N , conc.; fuming (90%)

Sodium hydroxide: 6N

Sodium chromate: 3 N

Sodium chloride: 4 N

Strontium nitrate carrier: 70 mg/ml

Barium nitrate carrier: 50 mg/ml

Procedure

1. Pour 70 cc of cation exchange resin into the glass column with the aid of distilled water.

2. Add 1 ml of strontium carrier and 1 ml of barium carrier to 500 ml of milk and mix well.

3. Place 500 ml of milk of homogeneous appearance into a glass reservoir. Let milk flow through the cation resin at a flow rate of 12 ml/min. Stop when just enough milk remains in column to cover resin. Discard effluent milk. Replace milk reservoir with separatory funnel containing approximately 200 ml of warm distilled water, and displace milk on column with water. Discard effluent.

4. Place 500 ml of 4N NaCl on top of column. Elute the absorbed cations from resin at a flow rate of 15 ml/min into 1 liter hot distilled water. Heat effluent during collection to 85°-95° C.

5. Add 100 ml of 3N Na_2CO_3 with stirring. Let precipitate settle while cooling in a cold water bath.

6. Decant supernate with care and transfer precipitate to glass centrifuge tube graduated to 40 ml. Centrifuge and decant supernate. (NOTE: Requires 4 to 6 centrifugations to complete this step.)

7. Wash precipitate twice with 30 ml distilled water. Centrifuge and decant.

8. Dissolve precipitate with 2 ml of conc. HNO_3. (NOTE: Add slowly with stirring to prevent excess bubbling from release of CO_2.)

9. Dilute solution to 9 ml with distilled water. Add slowly with extreme caution 31 ml of fuming HNO_3 (the ratio of fuming HNO_3 to water should be 3.5:1). Cool in ice bath with stirring for 5 to 10 min. Centrifuge and decant supernate. Drain centrifuge tube to remove excess HNO_3.

10. Dissolve precipitate with 3 to 4 ml of distilled water.

11. Increase to approximately pH 5 with 1 to 2 ml 6N NaOH. Adjust exactly with 2 ml of CH_3COONH_4 buffer. Check with pH paper.

12. Heat solution in a boiling water bath; add dropwise and with stirring 1 ml of Na_2CrO_4 to precipitate $BaCrO_4$. Centrifuge and decant supernate into a glass centrifuge tube, graduated to 40 ml. Discard the precipitate.

13. Dilute the solution to 9 ml with distilled water and add with extreme caution 31 ml of fuming HNO_3. Cool in ice bath with stirring. Centrifuge and decant supernate.

14. Dissolve strontium nitrate precipitate in a few drops of water and transfer to stainless steel planchets. Use 1 to 2 ml water to wash over.

15. Evaporate to dryness under heat lamps.

16. Count in beta counter within 1 hour of step No. 12.

17. Cover with 0.011" aluminum absorber and recount immediately.

Calibration of Counter

Pipet 1 or 2 ml of strontium-89 and strontium-90 solutions of known activity into separate 50 ml glass centrifuge tubes. Add 1 ml strontium carrier and 20 ml fuming (90%) nitric acid to each. Cool in ice bath and stir until cold. Centrifuge and discard solution. Dissolve precipitate in approximately 1 ml of water, transfer quantitatively to counting planchet with water, and dry. Count in beta counter. Recount after covering sample with 0.011" aluminum foil. The strontium-90 standard must be counted immediately to minimize the effect of yttrium-90 growth. The ratio of the count rates (uncovered) to the known disintegration rates gives the counting efficiencies of the counter, E_{Sr-89} and E_{Sr-90}. The ratio of count rates, covered to those uncovered, F_{Sr-89} and F_{Sr-90}, is used to calculate the fraction of each strontium

radionuclide in the sample. Values of "F" have been obtained for the strontium radionuclides on 2" dia, 0.020" thick, steel planchets with an internal proportional counter (IPC) and an anticoincidence end-window G-M counter. Three aluminum milk caps with a combined thickness of 0.011" (0.28 mm) were used as absorbers. Typical F values are:

Counter	F_{Sr-89}	F_{Sr-90}
IPC	0.38	0.078
G-M	0.43	0.076

Calculations

$$C_{Sr-90} = \frac{C_O F_{Sr-89} - C_A}{F_{Sr-89} - F_{Sr-90}}, \text{ and}$$

$$C_{Sr-89} = C_O - C_{Sr-90},$$

where C_O and C_A are the initial count and the recount with absorber, respectively.

$$\text{Strontium-90 (in } \mu\mu c/l) = \frac{C_{Sr-90}}{2.22\ ERV},$$

where R is the fractional recovery of the radioactive strontium in the procedure, V is the milk volume in liters, and E is the counter efficiency. A similar calculation is performed for strontium-89.

Comments

The recovery of strontium, R, was found to be 80 ± 5% in tracer studies; to save time and because of the approximate nature of the method, this recovery value, or one based on similar experiments, is preferred to actual measurement of strontium carrier. Retention of strontium on the resin column is 98 ± 2%, the other losses occurring during subsequent chemical separation steps. Liter volumes of milk may be analyzed by doubling the amount of resin, but keeping all other procedures and reagent volumes constant. The time required to analyze several samples simultaneously is approximately 5 hours. The accuracy with which strontium-90 can be distinguished from strontium-89 depends on the counting error of C_O and C_A.

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DETERMINATION OF IODINE-131, CESIUM-137, AND BARIUM-140 IN MILK BY GAMMA SPECTROSCOPY[1]

by

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Gamma scintillation spectroscopy is a particularly valuable technique in radionuclide analysis because it requires no sample preparation or chemical separations. This represents a considerable saving of labor and eliminates the possibility of error in processing. In quantitative applications, spectrometer stability with respect to high voltage, amplifier gain, and channel widths is critical. If a number of gamma-emitting nuclides are present, the complex spectrum must be resolved for quantitative measurement of each individual component.

Measurement of nuclides at the very low levels found in environmental samples imposes particularly stringent requirements in both instrumentation and spectrum interpretation. Since the nuclides of interest are present in such small quantities as to be barely recognizable above the background response of the detector, the measurement must be made for a considerable length of time to realize even fair counting statistics. For this, very good instrument stability is essential.

Since May 1957, analyses of the radionuclide content of milk at the Robert A. Taft Sanitary Engineering Center (5) have shown that the principal radionuclides found in milk are strontium-89, strontium-90, cesium-137, iodine-131, barium-140, potassium-40, and their daughters. Other radioisotopes ingested by the cow are eliminated by metabolic processes and do not reach the milk in significant quantities.

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[1] This work was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(49-5)-1288. It is a modification of the paper appearing in Talanta, 5:36-43 (1960).

[2] Present address: Monsanto Chemical Company Mound Laboratory, Miamisburg Ohio

[3] Present address: Northeastern Radiological Health Laboratory, Winchester, Massachusetts

Anderson (1) and Booker (2) have utilized gamma scintillation techniques in analyzing for cesium-137 and potassium-40 in dried milk. Because gamma emitters of short half-life were not present in this material, stringent spectral interference corrections were not necessary.

The method described below, which is similar to techniques used by others (3), was developed to permit the determination of iodine-131, cesium-137, and barium-140 in fluid milk entirely by gamma spectroscopy. The individual nuclide contributions to the gamma spectrum were separated by solution of simultaneous equations describing the spectral interferences. This technique does not concentrate the error in the nuclide of the lowest energy, as does the more common procedure of successive spectrum subtractions (6).

Development of the Method

The gamma spectrum obtained from a milk sample is a composite of individual spectra from cesium-137, iodine-131, barium-140, potassium-40, and instrument background. By measuring the spectrum of each of these separately, it was possible to determine the effect of each nuclide on the others.

The spectrum of a monoenergetic source as obtained with a scintillation detector consists of a Gaussian-shaped photopeak, at the full energy of the gamma ray, plus a Compton continuum from somewhat below the full energy to zero energy. In a mixture, consequently, a photopeak will be superimposed on the Compton region from all higher energy emitters. The extent to which a spectrum is masked by the Compton continua depends upon the number of higher-energy gamma emitters present and the quantity of each. The contributions of all higher-energy emitters must be subtracted from the gross spectrum in order to obtain the net spectrum of the emitter of lower energy. Direct spectral subtraction is reasonably satisfactory, although, as in all cases of successive subtractions, errors are cumulative.

In addition to this Compton interference, there is sometimes direct interference between photopeaks of two gamma emitters. In this case, straightforward subtraction is not possible, since neither spectrum has a characteristic region free of interference from the other. For example, iodine-131 has a minor photopeak at 0.64 Mev which interferes with the cesium-137 photopeak at 0.66 Mev, while the cesium-137 Compton continuum interferes with the main peak of iodine-131 (0.364 Mev). Similarly, the 1.60 Mev photopeak of lanthanum-140 is

often obscured in actual samples by the 1.46 Mev peak of potassium-40 present in the sample and in background.

For checking milk soon after its production, the lanthanum-140 daughter will not be in equilibrium with its barium-140 parent. Because the procedure depends on the presence of this barium-140 lanthanum-140 pair in the ratio actually to be encountered, the standards must reflect this situation.

The gross activity of each of the pertinent nuclides considered can be expressed analytically as:

$$G_I = I + C_I C + L_I L + K_I K + B_I \qquad (I^{131}) \qquad (1)$$

$$G_C = I_C I + C + L_C L + K_C K + B_C \qquad (Cs^{137}) \qquad (2)$$

$$G_L = I_L I + C_L C + L + K_L K + B_L \qquad (Ba\text{-}La^{140}) \qquad (3)$$

$$G_K = I_K I + C_K C + L_K L + K + B_K \qquad (K^{40}) \qquad (4)$$

The nomenclature for these equations is given in table 1.

Table 1.-Nomenclature for Equations (1-4)

Item	Spectral region for			
	K^{40}	I^{131}	Cs^{137}	$Ba\text{-}La^{140}$
Gross activity (cpm) in:	G_K	G_I	G_C	G_L
Background (cpm) in:	B_K	B_I	B_C	B_L
Fractional coefficient of K^{40} in:	1	K_I	K_C	K_L
Fractional coefficient of I^{131} in:	I_K	1	I_C	I_L
Fractional coefficient of Cs^{137} in:	C_K	C_I	1	C_L
Fractional coefficient of $Ba\text{-}La^{140}$ in:	L_K	L_I	L_C	1
Net activity (cpm) of each nuclide in its spectral region	K	I	C	L

The fractional coefficients, C_I, etc., are determined from the individual spectra as the ratio between the activity in the region of interest and that in the principal photopeak region. For example, in a pure cesium-137 spectrum, 32.4 counts in the iodine spectral region (0.32-0.40 Mev) are obtained for each 100 counts in the cesium spectral region (0.60-0.72 Mev). C_I, which accounts for the interference of cesium-137 in the iodine-131 region, is therefore equal to 0.324. Since the G's and B's are experimentally determined, the four equations (1-4) can be solved for the unknowns I, C, L, and K, the net counting rates. Once these net counting rates are known, the absolute quantity of each nuclide in the sample is readily determined from calibration data.

The necessity for extremely good stability throughout a spectrometer system is apparent, since drifts in amplifier gain, high voltage, and the like change appreciably the spectral regions covered by certain channels. The resulting variations in the fractional coefficients introduce error into the calculations of the net count of each nuclide. While the influence of drift is not fully known, a one-channel (20 Kev) shift in the location of the potassium-40 peak changes fractional coefficients for this nuclide about 8 percent.

It should be observed that the fractional coefficients are determined only once for the particular counter system employed. Day-to-day measurements of a cesium-137 standard have shown the constancy of coefficients over many months of operation. Analytical results obtained on mixtures of nuclides measured over several months further verify coefficient stability.

Materials

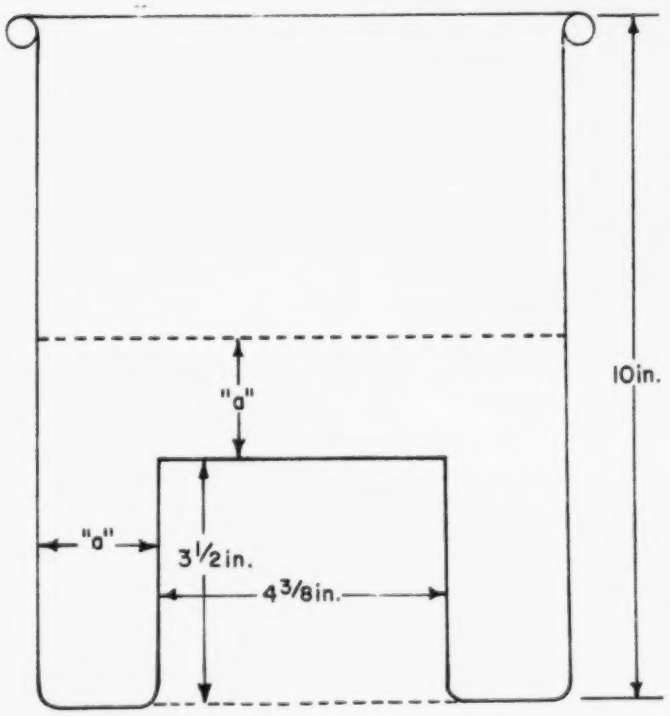
The basic instrument used in this method is the low level gamma spectrometer (4). It consists of a heavily shielded scintillation detector in association with a multichannel pulse height analyzer. The detector is a 4" x 4" solid NaI (Tl) crystal housed inside 6" of steel shielding.

Since the geometry of the sample grossly affects the spectral shape obtained, it was important to keep it constant in all work. Specially designed aluminum sample beakers (figure 1) surround the crystal for optimum and rigidly fixed geometry.

The cesium-137, iodine-131, and barium-lanthanum-140 used for calibration were purchased as certified standards or were standardized by conventional 4-pi beta counting at our laboratory.

Experimental

To determine the effect of each nuclide on the others, and to calibrate the spectrometer, the spectra of the pure individual isotopes were determined. To simulate a milk solution, a known quantity of the emitter was diluted to 3.5 liters with distilled water, suitable carrier was added, and precautions were taken to insure homogeneous distribution. After sodium chloride was added to approximate the density of milk, this solution was placed in one of the specially designed beakers and the nuclide spectrum was determined.



Volume	"a"
1-liter	3/4 in.
2-liters	1 1/3 in.
3.5 liters	1 17/20 in.

Figure 1.-Specially Designed Sample Beaker

Figures 2 and 3 are the spectral curves for iodine-131, cesium-137, barium-140-lanthanum-140, potassium-40, and background.

Suitable spectral regions (peak areas) were selected for each nuclide and are listed in table 2. Calculations of barium-140-lanthanum-140 are based on the 0.49 Mev gamma ray

Table 2.-Spectral Regions and Fractional Coefficients

Nuclide	E (Mev)	Spectral region energy (Mev)	Coefficient	Value of Coefficient
I^{131}	0.364	0.32-0.40	I_C	0.075
			I_L	0.025
			I_K	0
Cs^{137}	0.66	0.60-0.72	C_I	0.324
			C_L	0.186
			C_K	0
Ba^{140}-La^{140}	0.49	0.46-0.54	L_I	0.866
			L_C	0.313
			L_K	0.185
K^{40}	1.46	1.40-1.52	K_I	0.389
			K_C	0.300
			K_L	0.256

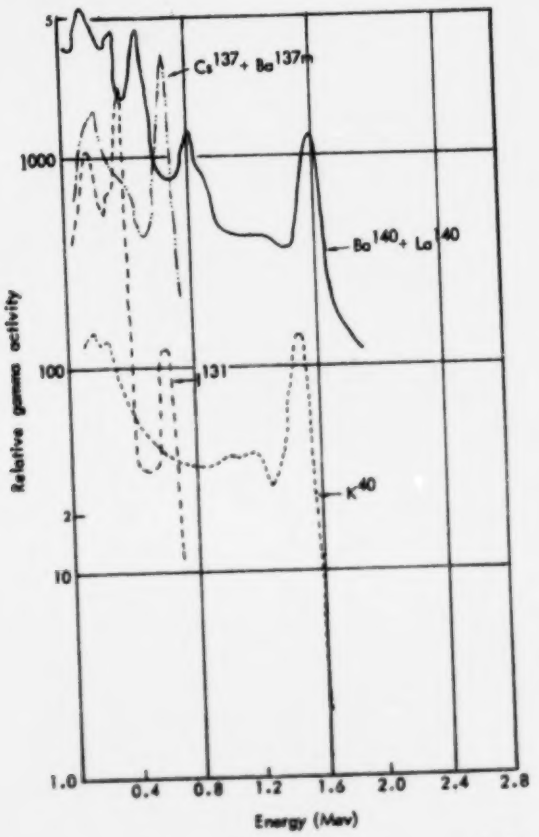


Figure 2.-Spectra of I^{131}, Cs + Ba^{137m}, Ba^{140} + La^{140}, and K^{40} on Low Level Gamma Spectrometer

which occurs in a portion of the spectrum relatively free from other nuclides. Once these regions have been chosen, the fractional coefficients for the interference of one nuclide with another are obtained from the spectra of the pure isotopes. These are also listed in table 2.

Analytical Procedure

A 3.5 liter sample in an aluminum or plastic beaker is placed on the detector, and the spectrometer is adjusted to cover the energy range between at least 0-2 Mev in 20 Kev channels. The spectrum is usually measured for 100 min, which gives the required sensitivity and precision and still permits measurements of an adequate number of samples. From the results, printed on standard adding machine tape, the values of the various G's of equations (1-4) are obtained. Background spectra are obtained in similar manner, using distilled water, usually over 1000 min. The B's of equations (1-4) are obtained from an average of the background spectra of an entire week.

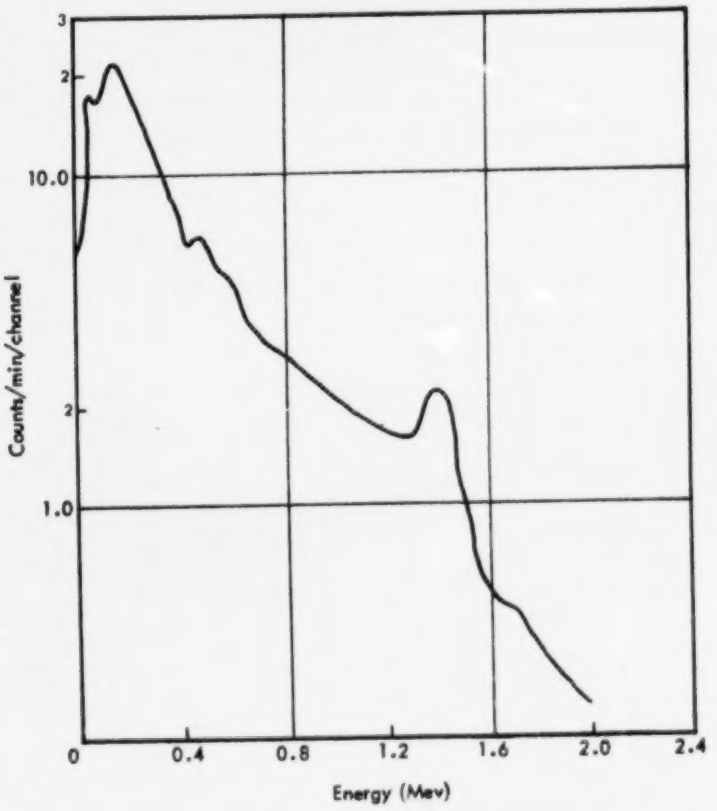


Figure 3.-Background Spectrum on Low Level Gamma Spectrometer

For ease of calculation, equations (1-4) are solved explicitly for I, C, and L, yielding the new equations (5), (6), and (7).

$$I = 1.034(G_I - B_I) - 0.812(G_L - B_L) - 0.183(G_C - B_C) - 0.139(G_K - B_K) \quad (5)$$

$$C = -0.074(G_I - B_I) - 0.226(G_L - B_L) + 1.066(G_C - B_C) - 0.233(G_K - B_K) \quad (6)$$

$$L = -0.013(G_I - B_I) + 1.115(G_L - B_L) - 0.203(G_C - B_C) - 0.219(G_K - B_K) \quad (7)$$

As a further convenience, equations (5), (6), and (7) have been programmed on an IBM 650 computer.

Evaluation

Solutions containing known amounts of cesium-137, iodine-131, barium-140-lanthanum-140, and potassium-40 were analyzed as described above. The first mixture studied contained amounts of cesium-137 and potassium-40 comparable to those found in routinely analyzed milk samples, with initial iodine-131 and barium-140-lanthanum-140 levels comparable to the highest values found during two years of operation. Analyses were repeated at various time intervals. Because of the decay of iodine-131 and barium-140-lanthanum-140 components, the sample represented a different nuclide mixture for each measurement. Results of these analyses are tabulated in the original paper (see footnote, p. 17).

The observed and known values of iodine-131 are in excellent agreement throughout, the difference being within 5% down to 40 μμc/l. The observed values for cesium-137 are, on the average, 10% higher than the actual levels. In the first two or three measurements, the cesium-137 photopeak was almost completely masked by the large quantity of iodine-131 present. Nevertheless, the mathematical solution eliminated this interference quite well. The values for barium-140 are slightly lower but are sufficiently accurate at these concentrations for all but the most exacting work. The iodine-131 errors become insignificant as the barium-140-lanthanum-140 concentration decreases. Deviations of "known" from "observed" values may in part be due to the ± 5% accuracy of the "known" value as a result of standardization. This would explain consistent deviations for a given nuclide.

Counting statistics alone cannot account for deviations of "observed" from "known" results in the above analyses. Slight instabilities in the equipment affect results, as already mentioned. In addition, the fractional coefficients are not known sufficiently well in all cases to ensure a uniform spread of results about an average close to the true value. Thus, iodine-131 values are not distributed uniformly about the true mean value of zero. Another possible source of error is correction for background. Day-to-day variation in background measurement is about 4% of the average value, about twice as much as can be attributed to statistical fluctuations. Although this variation is small, it nevertheless contributes to the overall errors.

Considering all these sources of error and the results obtained, the accuracy of the method is estimated to be ± 5-10 μμc/l between 0 and 100 μμc/l, and 5-10% at higher concentrations.

Coefficients were obtained not only for barium-140-lanthanum-140 in equilibrium, but with separated barium-140 into which lanthanum-140 had grown for a 25-hour period. The coefficients for L_I, L_C, and L_K for the non-equilibrium radionuclides differed by - 3%, + 13%, and - 27%, respectively. These differences affect the overall results but not to any large extent. For greater accuracy, if a large number of samples to be encountered will be less than one day old, coefficients and efficiency values can be obtained for barium-140 with an ingrowth of lanthanum-140 comparable to the milk samples to be analyzed.

Gamma spectroscopy offers a convenient technique for the simultaneous measurement of cesium-137, iodine-131, and barium-140 in milk. Many difficulties associated with radiochemical techniques, such as reagent interference in sequential chemical analysis or loss of material in concentration or procedural steps, are eliminated since no sample preparation is required. The gamma-emitting nuclides can be determined at concentrations above 10 μμc/l with an accuracy of 5-10 μμc/l for levels up to 100 μμc/l and about ± 5-10% at higher levels. Possibly this accuracy can be improved by the use of specialized equipment to provide more stable long-term operation.

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